CHARACTERIZATION OF THE ORGANIC MATTER
IN A WELL TO POORLY DRAINED
SEQUENCE OF SOILS

A Thesis
Submitted to
The Faculty of Graduate Studies and Research
University of Manitoba

In Partial Fulfillment
of the Requirements for the Degree
MASTER OF SCIENCE

by
Michael J. Capel
June 1968

ACKNOWLEDGEMENTS

The author wishes to thank:

Dr. M. A. Zwarich, Assistant Professor, Department of Soil Science, who suggested the investigation and under whose guidance it was carried out.

Dr. R. A. Hedlin, Head of the Department of Soil Science, for arranging financial assistance during the period of the investigation.

The staff of the Department of Soil Science for advice which, though not always acted upon, was greatly appreciated.

Mr. Mohammed Ali for assistance with laboratory analyses.

Miss Mary Ann Hildebrandt for typing the thesis.

ABSTRACT

The quantitative composition of the organic matter and functional group analysis of the humic acid fraction did not enable one to distinguish the organic matter of a well drained soil from that of associated soils of poorer drainage.

The amount of organic matter extracted by 0.5N NaOH was influenced by the degree of saturation of the exchange complex by Ca^{++} and Mg^{++}. The amount of humic acid extracted was influenced to a much greater extent than was the fulvic acid. Extrapolation of the results indicated that the amounts of humic and fulvic acids extracted would be similar in all the soils investigated if the effect of Ca^{++} and Mg^{++} was removed.

The humic acids were similar in their content of carboxyl and "phenolic" hydroxyl groups. Differences that did occur were between humic acids from different horizons rather than different soil types.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

PAGE

I INTRODUCTION

Gleysolic soils are defined by the N.S.S.C. (28) as soils saturated with water at one or more seasons, or artificially drained. The subsurface horizons usually have colors of low chroma and/or prominent mottles. During periods when the soils are not saturated, or if they are artificially drained, their classification becomes somewhat subjective. This difficulty arises because nearly every sub-group of the gleysolic order has a better drained equivalent and the separation is then based on the degree of gleization.

Since gleysolic soils are subjected to periods of saturation and support a vegetation different from that of better drained soils, it was felt that the organic matter of these soils might show quantitative and/or qualitative variations in the various fractions that could be utilized as differentiating criteria.

Studies of soil organic matter are complicated by the large number of generally inadequate techniques utilized, and when evaluating results, the methods utilized must be considered. In selecting the methods used in this investigation, the possibility of their adoption for routine analysis was given careful consideration.

Two well drained soils and four associated soils of poorer drainage were selected. All the soils had developed on moderately calcareous, medium textured till of similar origin, under similar macroclimatic conditions.

The principal objectives of this investigation were:

1. to determine the ratio of humic to fulvic acids;
2. to characterize the humic acids by functional group analysis;
3. to assess the value of these determinations as criteria for soil classification purposes.

II REVIEW OF THE LITERATURE

Introduction

The identification and characterization of the components of soil organic matter presents workers in this field with a formidable task (27). Broadbent (8) has stated that it would be surprising if soil organic matter everywhere had a common composition and Dubach and Mehta (12) have said that perhaps no two molecules of humic substances are alike.

The components of soil organic matter can conveniently be divided into two groups, namely, non-humic substances and humic substances (12). The non-humic substances are organic compounds present in undecayed plants and animal residues, products of their decomposition and products of microbial activity (23, p.45; 27). These substances belong to the relatively well defined groups of organic compounds found in living organisms, e.g. carbohydrates, proteins, fats, waxes, lignins, etc. The humic substances are defined by Felbeck (16) as those materials produced in soils that are either yellow or brown to black colored, acidic, polydisperse substances of relatively high molecular weight. Some workers (23, p.45; 42, p.8) extend the definition to include similar substances found in coals and decaying plant and animal residues, e.g. composts. The inclusion of substances found in coals has been questioned and some workers (10; 16) suggest that they be omitted from the definition until their identity has been clearly established.

Humic substances are generally divided into three classes on the basis of their solubility (16). These are as follows:

a) Fulvic acid:- soluble in alkali and acid and generally considered to be of relatively low molecular weight.

b) Humic acid:- soluble in alkali but insoluble in acid and generally considered to be of medium molecular weight.

c) Humin:- insoluble in alkali and acid, except under more drastic conditions than are normally employed to solubilize fulvic and humic acids. Generally considered to be the fraction with the highest molecular weight.

Although the present evidence indicates that fulvic acid may be chemically distinct from the other two classes (16), the difference between the humic acid and humin may be attributable to the strength of bonding to mineral matter (23, pp. 69- 74).

Felbeck (16) noted that the above definitions may give the impression that there are clear cut differences between non-humic and humic substances and the three classes of humic substances. Between non-humic and humic substances there exists a vast array of compounds produced by biological and/or chemical processes (23, p.45; 27; 42, pp. 5- 6). In the case of aromatic compounds such as lignins, degraded lignins, tannins and microbial metabolites, the line of separation from humic substances is impossible to define in theory or achieve in practice (12). Also there is a lack of distinction between the three classes of humic substances, their separation being based on rather generalized solubility properties.

The complexity of soil organic matter, the relatively small amounts in most soils and the difficulty of isolating it from the soil, have caused many problems in the study of this important fraction of the soil.

Isolation of Soil Organic Matter Fractions

"Chemical and physical information on an unknown substance is reliable only to the extent that it is obtained on a pure and homogeneous material. Humic substances have, therefore, to be, (1) extracted from the soil in an unaltered form, (2) purified by removal of the accompanying non-humic substances and (3) fractionated into homogeneous - in the ideal case, crystalline-components."

This statement by Dubach and Mehta (12) presents many problems, which, as yet, have not been overcome. At the present time the knowledge of the structural chemistry of humic substances is in the theoretical stage. With this limited information it is difficult to comply with the requirements set down by Dubach and Mehta. Thus, we may ask, how does one determine if an extracted humic substance is altered or not?, where is the dividing line between humic and non-humic substances?, what criteria is to be used to define homogeneity when fractionating humic substances?

In organic soils the humic substances are usually mixed with large quantities of non-humic substances, the proportions of the two being dependant upon the degree of decomposition. In this case the problem of obtaining pure samples of the humic substances is one of defining what constitutes each class of substances. In mineral soils the problem of non-humic substances as contaminants is not as serious, the humic substances constituting over fifty percent of the soil organic matter (12) and as high as eighty five to ninety percent (23, p.45). The problem that arises in this case is the presence of large amounts of mineral material, the organic matter content being no more than ten percent, by weight, in most soils (9, p.22). For studies on the mineral portion of these soils it is comparatively easy to destroy the organic matter without seriously affecting the nature of the mineral matter. However, at the moment, there is no easy way of destroying the mineral matter without affecting the organic matter (41).

The other approach to the problem is to remove the organic matter by dissolving it away from the mineral matter. It is this approach that has been used since the first attempts at isolating humic substances were carried out. Ideally all the organic matter should be dissolved, but no solvent capable of doing this has yet been found. There are exceptions to this statement, but they appear to be special cases. For example, Schnitzer and co-workers (38) were able to extract ninety six percent of the organic carbon of a Podzol B horizon using sodium hydroxide. The same reagent only extracted 24.8 percent of the organic carbon of the Ao horizon of the same soil. Further work on the extracted organic matter of the B horizon suggested that it consisted mainly of one component (43).

The difficulties of extracting the organic matter are caused by the fact that various components are combined with inorganic constituents and do not exist, to any extent, in a free state. Humic substances are known to form insoluble salts with polyvalent cations and also to interact with clay minerals (12; 26, p.182; 27). These reactions render some of the humic substances totally insoluble and others come into solution in combination with mineral impurities.

Methods of extracting and fractionating humic substances have been reviewed by several workers (5; 8; 12; 23, p.49; 26; 27; 41). Though the number of procedures described is very large, they differ mainly in operational details rather than basic principles. In fact, most methods can be placed in one of two groups, (a) those which involve the use of solutions of strong or weak alkalies and (b) those which involve the use of solutions of "complexing" salts (41). There are some methods which overlap the two groups because they involve the use of a solution of a "complexing" salt which is at a high pH. There are also some methods which do not fall in either group, e.g. the one involving the use of mineral acids (37).

The use of alkaline solutions to extract humic substances dates back to 1786 when the method was utilized by F. K. Achard (30, p.264). Since that time alkaline solutions have been the most widely used means of extracting humic substances. The most common reagent is a dilute solution of sodium hydroxide (24). The mechanism of the alkali solubilization of organic matter is explained by Russell; "...the high pH raises the electric charge on the humus particles through increasing the dissociation of hydrogen ions, and the hydroxyl ions compete more strongly than many of the humus colloids for the positively charged spots on the soil and clay particles;" (30, p.265). Other alkaline extracting reagents that have been used include ammonium hydroxide, sodium carbonate and sodium carbonate-bicarbonate solutions (30, p.265; 41). These extract less organic matter than sodium hydroxide due to the lower pH of the solution (30, p.265).

The use of solutions of "complexing" salts was prompted by the fears of some workers that alkaline solutions caused chemical alterations to the extracted organic matter. The opinions on this point are divided; some workers maintain that alkali extraction alters the humic substances (8; 41), whilst Russell (30, p.265) states that there is no clear evidence to support this. On the other hand, Kononova (23, p.50), on the basis of the results of several Russian workers, says that it has been shown that alkali extraction does not essentially alter the nature of the humic substances. The possibility of these criticisms being correct prompted Bremner and Lees (7) to try milder reagents. They used the salts of several organic and inorganic acids. Of the ones tested sodium pyrophosphate was the most effective, though generally it extracted less organic matter than sodium hydroxide.

The general principle underlying the use of these reagents is that the anions form insoluble precipitates or soluble complexes with the cations that keep the organic matter in an insoluble form (5; 41). Though many of these milder "complexing" salts have been tried (5; 41) none of them have the general efficiency of sodium hydroxide in terms of amount of organic matter extracted. The only condition under which they approach the efficiency of sodium hydroxide is when the humic substances are in combination solely with polyvalent cations, e.g. in the B horizons of sandy podzols (30, p.266).

A new approach has been the use of the Na-form of a chelating resin which was recommended by Bremner (6). This method was tried by Levesque and Schnitzer (25) in comparison with sodium hydroxide. They reached the conclusion that whilst the Na-resin may be more suitable for the extraction of metal-organic matter complexes, sodium hydroxide may be preferable if the ultimate requirement is a sample of purified organic matter.

When the efficiency of extraction is judged by the amount of organic matter solubilized, sodium hydroxide is the most efficient extracting reagent. For some soils, particularly those with high exchangeable calcium and calcium carbonate contents, the efficiency of sodium hydroxide can be enhanced by pretreating the soil with dilute acid. This will remove the cations responsible for keeping some of the organic matter in an insoluble sate. Kononova (23, p.50) has recommended this pretreatment, but it would appear that its use is far from being universal. The efficiency of sodium hydroxide has made it the most widely used extracting reagent for soil organic matter studies.

The extraction of soil organic matter with sodium hydroxide forms the basis of the classical fractionation procedure, namely the separation of the organic matter into humin, humic acid and fulvic acid. These three fractions were defined previously as the fraction insoluble in alkali (humin), the fraction soluble in alkali insoluble in acid (humic acid) and the fraction soluble in alkali and acid (fulvic acid). The fractionation was further extended with the introduction of other fractions such as crenic and apocrenic acids, α and β humus and hymatomelanic acid. These fractionations have been described by several workers (19; 23; 26; 27; 30; 42).

The use of the milder extracting reagents such as sodium pyrophosphate did not change this classical fractionation. The extract contains the humic and fulvic acid fractions, the organic matter left in the soil being, by definition, the humic fraction. Acidification of this extract results in the precipitation of some of the organic matter, the humic acid fraction. The pH to which the extract is acidified effects the amount of material precipitated but many investigators simply add an excess of acid (44). It is apparent from reading the literature that the humic-fulvic acid separation remains the most popular.

Other attempts at fractionation have been made. Dubach and Mehta (12) mention the following examples: precipitability with salts, polyvalent cations and quaternary N bases; electrophoresis; chromatography on paper, cellulose, starch, silica, Al_2O_3, anion exchange resins and cellulose derivatives; molecular weight distribution with ultracentrifugation and Sephadex gelfiltration. These methods bring about fractionation but the "fractions" are not distinct and grade into each other. This indicates the presence of a continuous series of constituents (12), and it appears that "fractions" obtained by one method can always be refractionated by another technique and this can be repeated endlessly (12; 16).

The introduction of such terms as humic and fulvic acid caused much confusion, a fact that was noted by Waksman (42, p.62) who felt justified in the idea of abandoning the whole nomenclature system used for humic substances. According to Waksman, the reason for the confusion was the lack of recognition that these names only represented preparations and not specific chemical compounds. That these names have little meaning has been shown by the fact that varying experimental procedure can result in different organic matter preparations although by definition they would have the same name. Variations such as strength and type of extracting reagent and the pH at which humic and fulvic acids are separated can cause differences in the preparation obtained (24; 44). The humic acid extracted from a soil by sodium hydroxide may be quite different from that extracted by sodium pyrophosphate.

Much of the work done in characterizing organic matter preparations is limited by the lack of precision in the extraction and fractionation procedures. Comparison of the results obtained by various workers is made difficult by the lack of any standardized method of obtaining organic matter preparations. The differences between, for example, humic acids of two soil types, obtained by different methods, may not be real differences but simply a product of the methods. The situation was summed up by Felbeck (16) when he said: "The confusing and often contradicting results that have been obtained are the direct result of the inadequacies of the techniques of extraction, fractionation and purification, degradation, and final isolation and characterization of the products obtained."

Characterization of Soil Organic Matter

Most of the work done on the characterization of organic matter has been carried out for the purpose of elucidating the structural chemistry of the various fractions. The methods of characterization, the results obtained and their meaning in relation to the structural chemistry of humic substances have been the subject of a critical review by Felbeck (16). Since the present investigation was not concerned with the structural chemistry of humic substances, the results of this type of work will only be considered where it is felt that they have a direct bearing on the problem being studied.

The quantitative and qualitative variations of the organic matter from different soil types have been studied systematically chiefly by Russian workers (26, p.163). The Russian work has been discussed by Joffe (21, pp.191 - 226) and more recently and fully by Kononova (23). In Canada the variations in the organic matter of a Podzol and Grey Wooded soil were studied by Schnitzer and Gupta (34) but the later work of Schnitzer and his various co-workers has been concerned with the variations in organic soils (31; 32; 33; 36).

The concept of geographical regularities in humus* formation that coincide with the main soil groups of the U.S.S.R. was proposed by Tyurin (23, p.239). Data obtained by Kononova (23, pp.240 - 272) confirmed

---

* The term humus as used in the Russian literature appears to be synonymous with the term humic substances as described earlier.

Tyurin's idea. The organic matter of the main soil groups was characterized by making the following determinations (23, p.240):

"1) The percentage of humus and nitrogen in the soil: where data on the volume-weight of the soil were available, the humus reserve and its distribution in the soil profile were calculated.

2) The reserve of plant residues and the nature of their distribution in the soil profile.

3) The composition of humus (by Tyurin's method) - the group of substances extractable with ethanol-benzene, the humic acids (free, linked with Ca and also with R_2O_3), the fulvic acids (substances remaining in the acid solution after the precipitation of humic acids) and the humic substances in the residue of the soil after the isolation of these groups were determined quantitatively.

4) The capacity of humic acids (as solutions of humates) for light extinction in the spectrophotometer and also their capacity for coagulation in the presence of electrolytes."

The methods used for these determinations have been described (23, pp.337-355).

The only criteria used for characterizing the nature of the humic acids were the light extinction of solutions of humates, and coagulation threshold values. These revealed marked differences in the humic acids from different soils (23, p.271). Characterization procedures, such as functional group analysis, had not been carried out extensively at the time Kononova's work was published (1961).

Outside the U.S.S.R. the work on soil organic matter does not seem to be well coordinated. This appears to be a result of the great variety of approaches utilized by workers in this field. The studies of Schnitzer and various co-workers represents one of the few attempts to relate organic matter characteristics to the soil type. They compared the humic and fulvic acids of a Podzol and a Grey Wooded soil and found very little difference (34). Though their earlier work was concerned with mineral soils, the later work has been concentrated on organic soils (31; 32; 33; 36). For this reason any comparison of the characteristics of organic matter from mineral soils with their later findings must be done with caution.

Functional group analysis and content of humic and fulvic acids have been related to degree of decomposition of organic soils (31; 32; 33). Differential thermogravimetric curves for organic soils were found to show well defined peaks. The heights of these peaks showed an inverse relationship with degree of humification (36).

Schnitzer and Gupta (35) consider functional group analysis as one of the most important ways of characterizing the reactivity of soil organic matter. Dubach and Mehta (12), however, have questioned the value of these determinations. Schnizer and co-workers have devoted most of their attention to carboxyl and phenolic and alcoholic hydroxyl groups because the reactive hydrogens of these groups are responsible for the exchange capacity of soil organic matter (35).

Variations in total organic matter and its distribution in the soil profile have been recognized as characteristic of different soil groups (8). These variations are utilized in soil classification, e.g. Canadian soil classification system (28). In this system the only use made of variations in the nature of the organic matter is in the separation of L, F and H horizons. The separation is made by visual estimation of the degree of decomposition.

III MATERIALS AND METHODS

Description of Soil Profiles

The soils used for this project were from the Erickson and Newdale associations. The two associations have developed on medium textured, moderately calcareous glacial till of similar origin and composition. The well drained soils of the Erickson association vary from Dark Grey Chernozemic to Dark Grey Wooded profile types. In the Newdale association the well drained soils are dominantly of the Orthic Black Chernozemic profile type, though the profile features indicate that some degradation has taken place. The soils of these associations have been fully described (13; 14).

Four soils of the Erickson association were sampled, two from poorly drained sites (sites A and B), one from an imperfectly drained site (site C) and one from a well drained sites (site D). Two soils of the Newdale association were sampled, one from a poorly drained site (site E) and the other from a well drained site (site F).

The following field descriptions of the profiles of these soils are based on the National Soil Survey Committee of Canada Proceedings (Laval University, Quebec. 1965) and the sub-group names were assigned on the basis of field observations.

Site A

Association:	Erickson.
Subgroup:	Fera Humic Gleysol (Virgin Site).
Location:	S.W. corner of 21-25-28 West of the Principal Meridian.
Vegetation:	Mainly sedges.
Parent Material:	Medium textured, moderately calcareous glacial till.

Topography: Depressional.

Drainage: Poorly drained.

Horizon	Depth(inches)	Description
L-F	6-3	Very dark grey brown (10YR3/2) organic layer.
H	3-0	Very dark grey brown (10YR3/2) organic layer, highly decomposed; diffuse, wavy boundary.
Aheg	0-13	Dark grey (10YR4/1) clay loam, grey (10YR5/1) when dry; moderate, medium platy structure; firm when moist; clear, wavy boundary.
Aeg	13-15	Olive grey (5Y4/2) clay loam, olive grey (5Y5/2) when dry; common yellowish red (5YR4/8) mottles, moderate, fine granular structure; firm when moist; diffuse, irregular boundary.
Bfg	15-27	Olive grey (5Y4/2) clay loam, olive grey (5Y5/2) when dry; many yellowish red (5YR4/8) mottles; massive structure; firm when moist; slight effervesence with HCl; diffuse, irregular boundary.
BCg	27-48	Olive grey (5Y4/2) clay, light olive grey (5Y6/2) when dry; common yellowish brown (10YR5/8) mottles; massive structure; firm when moist; slight to moderate effervesence with HCl; diffuse, irregular boundary.

Horizon	Depth(inches)	Description
Cg	48-72	Olive grey (5Y5/2) to olive (5Y5/3) clay, light olive grey (5Y6/2) when dry; common yellowish brown (10YR5/6) mottles; massive structure; moderate effervesence with HCl; occasional lime streaks or patches.

Site B

Association: Erickson

Subgroup: Low Humic Eluviated Gleysol (Virgin Site)

Location: S.W. corner of 21-25-28 West of the Principal Meridian.

Vegetation: Willow, dogwood, meadow grasses.

Parent Material: Medium textured, moderately calcareous glacial till.

Topography: Depressional, about two feet higher than Site A.

Drainage: Poorly drained.

Horizon	Depth(inches)	Description
L-F	4-1	Black (10YR2/1) leaf mat.
H	1-0	Black (10YR2/1) well decomposed organic layer; clear, wavy boundary.
Aheg	0-3	Very dark grey (10YR3/1) loam, dark grey (10YR4/1) when dry; weak, medium platy structure; friable when moist; clear, wavy boundary.
Aeg	3-9	Dark grey (10YR4/1) loam, grey (10YR6/1)

Horizon	Depth(inches)	Description
		when dry; moderate, medium platy structure; friable when moist; clear wavy boundary.
Btg	9-16	Dark grey (10YR4/1) clay, grey (10YR5/1) when dry; dark reddish brown (2.5YR3/4) mottles; moderate, fine granular structure; very firm when moist; diffuse, wavy boundary.
BCg	16-30	Dark grey (5Y4/1) clay loam, grey (5Y5/1) when dry; moderate, fine granular structure; firm when moist; diffuse, wavy boundary.
C1g	30-42	Dark grey (5Y4/1) loam, grey (5Y5/1) when dry; pseudo-fragmentary structure; firm when moist; slight effervesence with HCl; diffuse, wavy boundary.
C2g	42-60	Light olive brown (2.5Y5/4) loam, light yellowish brown (2.5Y6/4) when dry; structureless; firm when moist; slight effervesence with HCl.

Site C

Association:	Erickson
Subgroup:	Gleyed Grey Wooded (Virgin Site)
Location:	S.E. corner of 17-25-28 West of the Principal Meridian.
Vegetation:	Mainly aspen with some balsam and willow.

Parent Material: Medium textured, moderately calcareous glacial till.

Topography: Depressional.

Drainage: Imperfectly drained.

Horizon	Depth(inches)	Description
L-H	3-0	Black (10YR2/1) leaf mat; abrupt smooth boundary.
Ahe	0-2	Very dark grey (10YR3/1) silty clay loam, dark grey (10YR4/1) when dry; medium, fine granular structure; friable when moist; clear, wavy boundary.
Ae	2-7	Light grey (10YR7/1) silt loam, light grey (10YR7/1) when dry; strong, medium platy structure; friable when moist; diffuse, wavy boundary.
ABgj	7-9	Dark grey (10YR4/1) loam, grey (10YR5/1) when dry; dark yellowish brown (10YR4/4) mottles; moderate, medium granular structure; firm when moist; diffuse, wavy boundary.
BAg	9-12	Dark grey (10YR4/1) clay loam, grey (10YR5/1) when dry; moderate, medium granular structure; firm when moist; diffuse, wavy boundary.
Btgl	12-22	Dark grey (10YR4/1) clay, grey (10YR5/1) when dry; weak, medium prismatic structure; very firm when moist; diffuse,

Horizon	Depth(inches)	Description
		irregular boundary.
Btg2	22-36	Very dark grey (10YR3/1) to dark grey (10YR4/1) clay; dark grey (10YR4/1) when dry; strong, medium prismatic structure; very firm when moist; diffuse, irregular boundary.
BCg	36-46	Dark yellowish brown (10YR4/5) to light grey (10YR7/1) clay loam, grey (10YR5/1) when dry; reddish brown (5YR4/4) mottles; strong, fine blocky structure; very firm when moist; slight effervesence with HCl; diffuse, broken boundary.
Cg	46-54	Light yellowish brown (10YR6/4) to yellowish brown (10YR5/4) loam, very pale brown when dry; strong, medium blocky structure; very firm when moist; slight effervesence with HCl.

At site C a sample of the Ap horizon (site C1) of the cultivated form of this soil was taken, about 25 feet from site C. Another sample (site C2) was taken about 200 feet from site C. This was also on Ap horizon, though the profile was an Orthic Dark Grey. The site was several feet higher than site C.

Site D

Association:	Erickson.
Subgroup:	Orthic Dark Grey (Virgin Site).

Location: S.W. corner of 21-25-28 West of the Principal Meridian.

Vegetation: Aspen, choke cherry and various grasses.

Parent Material: Medium textured, moderately calcareous glacial till.

Topography: 2% slope.

Drainage: Well drained.

Horizon	Depth(inches)	Description
L	2½-2	Very dark brown (10YR2/2) leaf mat; abrupt, wavy boundary.
F-H	2-0	Very dark brown (10YR2/2)moderately to well decomposed organic layer; abrupt; wavy boundary.
Ahe	0-7	Very dark brown (10YR2/2) loam, very dark grey brown (10YR4/1) when dry; moderate, medium granular structure; friable when moist, slightly hard when dry; abrupt, wavy boundary.
Bt	7-17	Dark brown (10YR3/3) clay, brown to dark brown (10YR4/3) when dry; moderate, medium blocky structure; firm when moist, hard when dry; clear, wavy boundary.
BC	17-21	Brown to dark brown (10YR4/3) clay loam, brown (10YR5/3) when dry; moderate, fine subangular blocky structure; friable when moist; slightly hard when dry; slight effervesence with HCl; clear, wavy boundary.

Horizon	Depth(inches)	Description
C1	21-25	Yellowish brown (10YR5/4) clay loam, light brownish grey (10YR6/2) when dry; moderate, fine subangular blocky structure; very friable when moist; slightly hard when dry; strong effervesence with HCl; gradual, wavy boundary.
Cca	25-29	Pale brown (10YR6/3) clay loam, light grey (10YR7/2) when dry; moderate, fine subangular blocky structure; very friable when moist, slightly hard when dry; violent effervesence with HCl; gradual, wavy boundary.
C2	29+	Olive (5Y5/3) (moist and dry) clay loam; weak, fine sugangular blocky structure; very friable when moist, slightly hard when dry; strong effervesence with HCl.

Site E

Association:	Newdale.
Subgroup:	Rego Humic Gleysol (Virgin site).
Location:	S.W. quarter of 27-15-19 West of the Principal Meridian.
Vegetation:	Spangle top.
Parent Material:	Medium textured, moderately calcareous glacial till.
Topography:	Depressional.
Drainage:	Poorly drained.

Horizon	Depth(inches)	Description
L-F*	4-0	Very dark grey brown (10YR3/2) organic layer; mainly composed of leaves and roots; lower portion has high mineral content; clear, wavy boundary.
Ahegl	0-2	Very dark grey brown (10YR3/2) loam, dark grey (10YR4/1) when dry; common yellowish brown mottles (10YR5/8 moist, 5/6 dry); weak, fine platy structure; very friable when moist, soft when dry; gradual, smooth boundary.
Aheg2	2-6	Very dark brown (10YR3/2 moist and dry) loam; common yellowish brown mottles (10YR5/8 moist, 5/6 dry); moderate, fine platy structure breaking to moderate medium granular; very friable when moist, soft when dry; clear, smooth boundary.
Ahgl	6-12	Very dark grey (10YR3/1) to black (10YR2/1) clay loam, dark grey (10YR4/1) when dry; few mottles; moderate, medium prismatic structure breaking to strong medium platy; friable when moist, slightly hard when dry; gradual smooth boundary.

---

* There was no H horizon. It appeared that the vegetation was burnt off regularly, so that the L-F layer was of fairly recent origin and relatively undecomposed.

Horizon	Depth(inches)	Description
Ahg2	12-18	Black (10YR2/1) clay loam, very dark grey brown (10YR3/2) when dry; few mottles; moderate, medium prismatic structure, breaking to strong, medium platy; friable when moist, slightly hard when dry; gradual, smooth boundary.
Ahg3	18-28	Black (10YR2/1) clay loam, very dark grey brown (10YR3/2) when dry; few mottles; moderate, medium platy structure; firm when moist, hard when dry; gradual, smooth boundary.
ACg1	28-38	Black (10YR2/1) to very dark grey (10YR3/1) clay, grey (10YR5/1) when dry; pockets of olive grey (5Y5/2) material; massive structure, breaking to moderate, fine to medium granular; firm when moist, hard when dry; gradual, wavy boundary.
ACg2	38-48	Very dark grey (10YR3/1) clay, grey (10YR5/1) when dry; pockets of olive grey (5Y5/2) material, massive structure, breaking to moderate, medium granular; firm when moist, hard when dry; gradual, wavy boundary.
Cg1	48-60	Olive (5Y4/2) clay, pale olive (5Y6/3) when dry; mottles and pockets of very dark grey (10YR3/1) material; massive

Horizon	Depth(inches)	Description
		structure, breaking to moderate, medium granular; firm when moist, very hard when dry; gradual, wavy boundary.
Cg2	60-84+	Dark brown to brown (10YR4/3) clay loam, light brownish grey (10YR6/2) when dry; mottles and pockets of very dark grey (10YR3/1) material; massive structure, breaking to moderate, medium granular, firm when moist, very hard when dry; slight effervesence with HCl.

Site F

Association:	Newdale.
Subgroup:	Orthic Black (Virgin site).
Location:	S.W. quarter 27-15-19 West of the Principal Meridian.
Vegetation:	Western snowberry, blue grass, awned wheat grass.
Parent Material:	Medium textured, moderately calcareous glacial till.
Topography:	2% slope.
Drainage:	Well drained.

Horizon	Depth(inches)	Description
L-H	1-0	Very dark brown (10YR2/2) leaf mat; clear, wavy boundary.
Ah	0-7	Black (10YR2/1) loam, very dark brown

Horizon	Depth(inches)	Description
		(10YR2/2) when dry; weak, medium prismatic structure, breaking to moderate medium granular; very friable when moist, slightly hard when dry; gradual, wavy boundary.
Btj	7-13	Very dark greyish brown (10YR3/2) clay loam dark greyish brown (10YR4/2) when dry; moderate, medium subangular blocky structure; friable when moist, hard when dry; gradual, wavy boundary.
BC	13-17	Dark greyish brown (10YR4/2) clay loam, greyish brown (10YR5/2) when dry; moderate, medium subangular blocky structure; friable when moist, hard when dry; slight effervesence with HCl; gradual, wavy boundary.
C1	17-22	Dark greyish brown (10YR4/2) loam, greyish brown (10YR5/2) when dry; moderate, medium granular structure; friable when moist, slightly hard when dry; strong effervesence with HCl; gradual, wavy boundary.
Cca	22-26	Dark brown to brown (10YR4/3) loam, grey to light grey (10YR6/1) when dry; moderate, fine granular structure; friable when moist, slightly hard when dry; violent effervesence with HCl; gradual, wavy boundary.
C2	22-36+	Dark greyish brown (10YR4/2) loam, greyish brown (10YR5/2) when dry; moderate, fine

Horizon	Depth(inches)	Description
		granular structure; friable when moist, slightly hard when dry; strong effervescence with HCl.

Preparation of Samples

The horizons used for the investigation were as follows:

Site A	L-F, H, Aheg.
Site B	L-F, H, Aheg, Aeg.
Site C	L-H, Ahe.
Site C1	Ap.
Site C2	Ap.
Site D	L, F-H, Ahe.
Site E	L-F, Ahegl, Aheg2, Ahgl, Ahg2, Ahg3.
Site F	L-H, Ah.

The soils were air-dried and ground to pass a 2 mm sieve. Unless otherwise stated all analyses were carried out on less than 2 mm material.

Analytical Procedures

Extraction, fractionation and purification of humic and fulvic acids. Although the majority of methods used for the extraction of soil organic matter are based on one of two principles, there is no universally accepted procedure. The method adopted in the investigation for the extraction and subsequent fractionation and purification of organic matter was based on methods described by Schnitzer and Gupta (34). These methods were used to extract, fractionate and purify the organic matter of a Grey Wooded Soil. It was felt that by using similar methods meaningful comparisons could be made between the results obtained and the results of Schnitzer and co-workers.

The organic matter was extracted using 0.5N NaOH and a soil: extractant ratio of 1:10 wt./vol. The soil, ground to pass a 0.5 mm sieve, was placed in a plastic bottle, the weight of soil used being dependant upon the content of organic matter. The appropriate volume of NaOH was added, the air in the bottle displaced by nitrogen and the bottle shaken for twenty four hours. After centrifugation at 2,000 r.p.m. for ten minutes the supernatant was poured off and adjusted to pH 2.0 by adding dilute HCl. The resulting precipitate was separated by centrifugation and washed into dialysis bags. The suspension in the bags was acidified by adding dilute HCl and dialysed against distilled water. The water was changed at frequent intervals and dialysis continued until the water was free of chlorides (tested with $AgNO_3$ solution).

When dialysis was complete the suspension was placed in a large evaporating dish and evaporated until it formed a gel. This was then shaken with dilute HCl - HF solution for three hours to reduce the ash content of the material. The HCl - HF solution was prepared by mixing 5 ml concentrated HCl and 5 ml of 56% HF and diluting it to one litre with distilled water. The amount of HCl - HF solution used was varied according to the amount of material so that an approximate ratio of 250 ml solution per gram of dry material was maintained. Following the HCl - HF treatment, the suspension was filtered, the precipitate washed until free of chlorides and dried. The drying was done using infra-red heat lamps and fans to keep the air moving over the samples. The dried samples were ground until maximum particle size was about 1 mm and stored in bottles in a desiccator containing P_2O_5 until used. This material is referred to as Humic Acid.

The supernatant obtained upon acidification of the NaOH extract contained the organic matter soluble at pH 2.0. This was purified by passing it twice over large columns of Rexyn 101 (H) cation exchange resin, after which it was dried by the method used for drying the humic acid samples. The organic matter was taken up in 1 : 1 methanol-acetone mixture, filtered and the filtrate evaporated to dryness. The residue was taken up in 0.5N NaOH, passed immediately over an hydrogen saturated exchange resin and evaporated to dryness. This material is referred to as Fulvic Acid.

Ash content of humic acids. The ash contents of the humic acids were determined by igniting one gram samples in a muffle furnace at 850° C for one half hour (2).

Extractable carbon and proportions in the humic and fulvic acid fractions. A ten gram sample of soil, ground to pass a 0.5 mm sieve, was placed in a 200 ml centrifuge bottle and 100 ml of 0.5N NaOH were added. For the Aeg horizon of site B, a fifteen gram sample and 150 ml of NaOH were used. The air in the bottle was displaced with nitrogen, shaken for twenty-four hours and then centrifuged at 2,000 r.p.m. for ten minutes. An aliquot of the supernatant was pipetted into a 100 ml centrifuge tube, the size of the aliquot being dependant upon the organic matter content of the extract. This was calculated assuming approximately twenty percent of the organic carbon was extracted from the soil.

The extract was acidified to pH 2.0 with dilute H_2SO_4 because the chloride ions from HCl would interfere with the determination of organic carbon. The humic acid fraction was allowed to coagulate and the suspension was centrifuged at 2,000 r.p.m. for twenty minutes. The supernatant, the fulvic acid fraction, was poured off into a 400 ml beaker, the humic acid washed twice with dilute H_2SO_4 and the washings added to the fulvic acid fraction. The humic acid was transferred to a 400 ml beaker and it, and the fulvic acid fraction, were evaporated to near dryness. The carbon contents of each fraction were determined by the method described later.

Functional group analyses. Carboxyl groups were determined by the calcium acetate method described by Schnitzer and Gupta (35). "Total acidity" was determined by the barium hydroxide method described by Schnitzer and Gupta (35) with the following modifications: (a) the weight of humic acid used was 100 - 200 mg; (b) 10 ml of $Ba(OH)_2$ were added; (c) the titration done with 0.3N HCl. These changes were made so that the difference between blanks and titration values became greater, thus reducing errors. The titration was done using phenolphthalein indicator instead of potentiometrically because of troubles that developed with the calomel electrode. After five or six titrations the pH meter started to give incorrect readings. The cause of this was found to be the calomel electrode. It is possible that $Ba(OH)_2$ diffused into the sintered glass plug at the end of the electrode and on exposure to the air precipitated as $BaCO_3$ which blocked the plug. The electrode could be made to function properly if it was soaked for several hours in dilute HCl.

"Phenolic" hydroxyl groups are assumed to be the difference between "total acidity" and carboxyl group content (35).

Organic carbon. Organic carbon was determined by the Walkley-Black method described by Allison (1). The method was modified to the extent that the titrations were done potentiometrically instead of using an indicator as described. A recovery factor of 75% was used in the calculation (1).

Total organic matter. Total organic matter was determined by multiplying percent organic carbon by 1.72 (20, p.221). This method was compared with loss on ignition and loss on peroxide treatment and seemed to be the most acceptable. For a comparison of the three methods see Appendix.

Mechanical analysis. Mechanical analysis was done by the pipette method. The procedure was basically that described by Kilmer and Alexander (22).

Cation exchange capacity and exchangeable calcium and magnesium. Cation exchange capacities were determined by the ammonium acetate method described by Atkinson *et al* (2). Calcium and magnesium in the ammonium acetate solution obtained from cation exchange capacity determinations were determined by titration with EDTA (18).

Soil reaction and lime potential. Soil pH was determined on a saturated paste using glass-calomel electrodes.

Lime potential was determined by measuring the pH of a suspension of soil in 0.01M $CaCl_2$ solution (1 : 2 soil/solution ratio) and subtracting 1.14 from the value (39).

IV RESULTS AND DISCUSSION

Extractable Carbon, and Humic Acid Carbon : Fulvic Acid Carbon Ratios.

The values for percent carbon extracted, and the proportions of carbon as humic and fulvic acids, do not show any apparent trends (Table I). The percentages of carbon extracted as fulvic acid have a narrower range (6.10 - 16.9%) than the equivalent values for humic acid (0.84 - 30.2%). This suggests that most of the variability in percent carbon extracted is associated with the humic acid fraction. In some cases the amount of carbon as fulvic acid was as high as that in the humic acid fraction. However when the soils were extracted to obtain material for functional group analysis only very small amounts of fulvic acid were obtained. The substantial loss of fulvic acid probably occurred during the passage of the solution of fulvic acid over an ion exchange resin. Loss of material during this procedure has been reported by Dubach and Mehta (12). The small yields of purified fulvic acid precluded further analysis of this fraction.

Variations in the extractability of soil organic matter reflect not only differences in its nature but also in its interactions with the inorganic fraction of the soil. Two of the major interactions affecting the solubility of humic substances occur with clay minerals and polyvalent cations (12). It is reasonable to assume that the mineralogy of the clay fraction is the same in all the soils investigated so the percent clay should indicate any effect that the clay is having on the extraction. In the present investigation there appeared to be no relationship between clay content and extractability of carbon (Tables I and II). This is especially noticeable in the Rego Humic Gleysol. The clay contents of the mineral horizons are about the same, whereas the percent carbon extracted

TABLE I

PERCENT SOIL ORGANIC CARBON EXTRACTED, PERCENT SOIL ORGANIC CARBON EXTRACTED AS HUMIC AND FULVIC ACIDS AND RATIO OF HUMIC ACID CARBON TO FULVIC ACID CARBON.

Profile Type	Horizon	% Soil O.C. Extracted	% Soil O.C. Extracted as Humic Acid	% Soil O.C. Extracted as Fulvic Acid	$\frac{\text{H.A.C.}}{\text{F.A.C.}}$ *
Fera Humic Gleysol	L-F	37.8	27.2	10.6	2.56
	H	41.3	29.2	12.1	2.41
	Aheg	32.1	18.4	13.7	1.33
Low Humic Eluviated Gleysol	L-F	26.2	13.0	13.2	0.99
	H	33.6	22.9	10.7	2.15
	Aheg	31.7	21.7	10.0	2.17
	Aeg	11.5	0.84	10.6	0.08
Gleyed Grey Wooded	L-H	21.0	10.7	10.3	1.04
	Ahe	42.2	30.2	12.0	2.52
Gleyed Grey Wooded	Ap	40.2	25.1	15.1	1.67
Orthic Dark Grey	Ap	18.3	9.70	8.60	1.12
Orthic Dark Grey	L	25.0	13.7	11.3	1.21
	F-H	29.4	17.5	11.9	1.47
	Ahe	31.0	15.3	15.7	0.98
Rego Humic Gleysol	L-F	44.6	27.7	16.9	1.64
	Aheg1	32.1	16.9	15.2	1.11
	Aheg2	27.0	13.2	13.7	0.96
	Ahg1	19.7	10.0	9.67	1.03
	Ahg2	14.2	6.52	7.70	0.85
	Ahg3	10.5	4.38	6.10	0.72
Orthic Black	L-H	22.0	12.3	9.68	1.27
	Ah	18.9	9.21	9.72	0.95

* $\frac{\text{H.A.C.}}{\text{F.A.C.}} = \frac{\text{Humic Acid Carbon}}{\text{Fulvic Acid Carbon}}$

TABLE II

MECHANICAL ANALYSIS OF SOME HORIZONS

Profile Type	Profile	Sand %	Silt %	Clay %
Fera Humic Gleysol	H	21.3	47.1	31.6
	Aheg	34.9	35.5	29.6
Low Humic Eluviated Gleysol	H	17.2	51.0	31.8
	Aheg	17.6	53.7	28.7
Gleyed Grey Wooded	Ahe	17.2	49.1	33.7
Gleyed Grey Wooded	Ap	36.2	45.4	18.4
Orthic Dark Grey	Ap	42.8	30.7	26.6
Orthic Dark Grey	Ahe	38.2	33.3	28.5
Rego Humic Gleysol	Aheg1	21.3	41.1	37.7
	Aheg2	21.1	41.5	37.4
	Ahg1	14.2	48.2	37.6
	Ahg2	21.3	42.2	36.5
	Ahg3	22.8	40.3	36.8
Orthic Black	Ah	38.4	31.3	30.3

varies from 32.1 percent in the Ahel to 10.5 percent in the Ah3.

The pH values for the soils (Table III) suggested that the exchange complex was saturated with varying amounts of bases and, because of the nature of the parent material, these would be mainly calcium and magnesium. Since the degree of saturation of organic matter with Ca^{++} affects its solubility (12) and Mg^{++} probably has a similar effect, this seemed to be a possible explanation for the variations in extractability. Lime potential was measured as an approximate indication of the degree of base saturation (Table III) and its relationship to percent carbon extracted is shown in Figure 1. There is a general tendency for extractability to increase as lime potential decreases (i.e. as base saturation decreases). Since degree of base saturation appeared to have affected the extractability of carbon, the percent saturation of the exchange complex with Ca^{++} and Mg^{++} was determined (Table IV).

The effect of percent Ca^{++} plus Mg^{++} saturation on the extractability is shown by Figure 2. The curve is sigmoid-like and tends to level off with decreasing Ca^{++} plus Mg^{++} saturation. It would seem that the level portion represents the maximum extractable carbon if Ca^{++} plus Mg^{++} are not affecting the extraction of organic matter with NaOH. The minimum extractable carbon when Ca^{++} plus Mg^{++} saturation is one hundred percent is probably the carbon present mainly as fulvic acid since the solubility of this fraction is not greatly affected by the presence of Ca^{++} (23, p.92). It can be seen that the solubility of the organic matter is affected when the percent Ca^{++} plus Mg^{++} saturation approaches 75 percent and the maximum effect is reached as it approaches 100 percent. There is a critical region at approximately 90 percent saturation where small changes in percent Ca^{++} plus Mg^{++} saturation seem to have a marked

TABLE III

pH AND LIME POTENTIAL.

Profile Type	Horizon	pH	Lime Potential
Fera Humic Gleysol	L-F	6.0	4.36
	H	5.9	4.16
	Aheg	6.3	4.66
Low Humic Eluviated Gleysol	L-F	6.6	5.11
	H	5.8	4.16
	Aheg	5.9	4.21
	Aeg	6.2	4.76
Gleyed Grey Wooded	L-H	5.7	4.16
	Ahe	5.2	3.36
Gleyed Grey Wooded	Ap	5.7	4.16
Orthic Dark Grey	Ap	6.9	5.41
Orthic Dark Grey	L	6.3	4.81
	F-H	6.6	5.16
	Ahe	6.1	4.46
Rego Humic Gleysol	L-F	5.1	3.61
	Ahegl	5.6	4.26
	Aheg2	5.8	4.36
	Ahgl	6.2	4.66
	Ahg2	6.2	4.81
	Ahg3	6.4	4.91
Orthic Black	L-H	6.5	4.91
	Ah	6.6	4.96

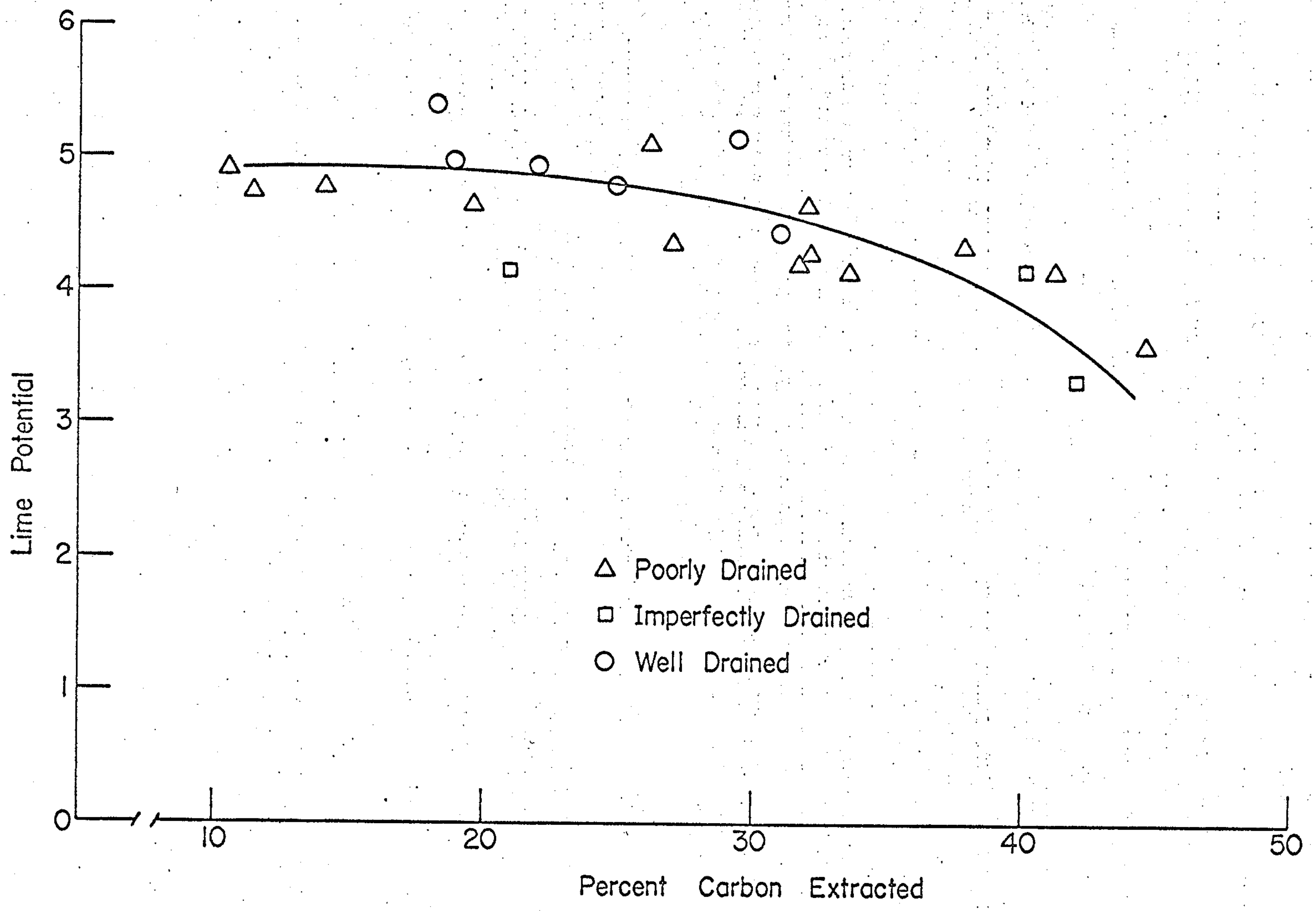

Figure 1 - RELATIONSHIP BETWEEN LIME POTENTIAL AND EXTRACTABLE CARBON.

TABLE IV

CATION EXCHANGE CAPACITY AND EXCHANGEABLE CALCIUM AND MAGNESIUM.

Profile Type	Horizon	C.E.C. me/100g	me/100g Exchangeable		% Saturation with Ca^{++} + Mg^{++}
			Calcium	Magnesium	
Fera Humic Gleysol	L-F	45.8	28.8	9.65	84.0
	H	38.5	21.3	6.57	72.4
	Aheg	24.0	15.4	5.92	88.7
Low Humic Eluviated Gleysol	L-F	77.5	59.5	16.7	98.4
	H	51.5	35.5	10.4	89.1
	Aheg	30.9	20.4	5.82	84.7
	Aeg	21.2	14.3	5.12	91.5
Gleyed Grey Wooded	L-H	68.1	50.2	9.87	88.2
	Ahe	35.6	16.8	3.67	57.5
Gleyed Grey Wooded	Ap	15.5	11.2	1.82	83.5
Orthic Dark Grey	Ap	28.5	25.0	3.27	98.9
Orthic Dark Grey	L	72.6	52.4	14.9	92.5
	F-H	75.2	60.8	13.7	98.9
	Ahe	24.4	16.9	3.77	84.7
Rego Humic Gleysol	L-F	42.3	22.6	6.77	69.4
	Ahegl	28.6	17.6	7.97	89.4
	Aheg2	27.6	17.0	8.22	91.2
	Ahgl	30.2	19.3	8.12	90.9
	Ahg2	29.2	19.4	7.57	92.4
	Ahg3	28.4	19.1	7.90	94.8
Orthic Black	L-H	50.3	35.8	10.5	91.8
	Ah	32.0	24.3	6.09	95.2

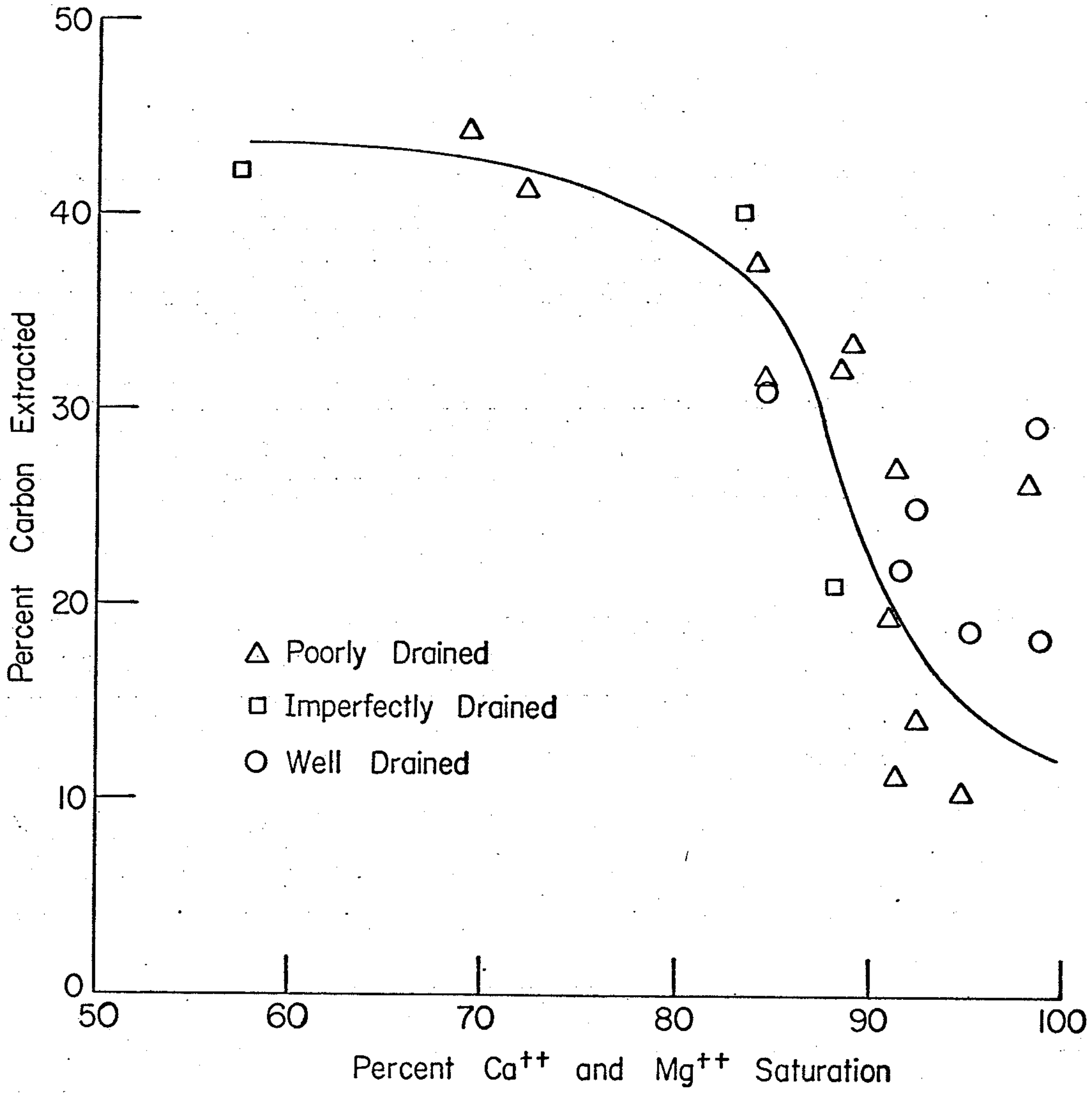

Figure 2 - EFFECT OF Ca^{++} AND Mg^{++} SATURATION OF EXCHANGE COMPLEX ON AMOUNT OF CARBON EXTRACTED.

effect on the extractability of the organic matter. The curve represents an average of the situation that exists in the soils investigated and would probably only hold for similar soils. It is noticeable that the placement of the points about the curve does not show any differentiation between soils of different drainage.

If percent carbon extracted as humic acid and percent carbon extracted as fulvic acid are considered independently, in relation to percent Ca^{++} plus Mg^{++} saturation, it can be seen that the humic acid is influenced the most (Figures 3a and 3b). There is a slight tendency for the percent carbon as fulvic acid to decline as Ca^{++} plus Mg^{++} saturation increases (Figure 3a) but there is very marked decrease in carbon as humic acid (Figure 3b). This is in agreement with the coagulation properties of humic and fulvic acids, given by Kononova (23, p.92). Calculation of percent extractable humic acid in the total organic matter (Table V) did not alter the shape of Figure 3b which indicates that carbon is a good index for measuring amounts of humic acid.

If one is justified in extrapolation of the curves to a point where Ca^{++} plus Mg^{++} saturation is low enough to have little effect (i.e. where the curves level off).the percent carbon as humic and fulvic acid are approximately thirty and fifteen percent, respectively. The value for humic acid is in reasonable agreement with the average value given by Kononova for soils that appear to be developed under similar climatic conditions and from similar parent materials to those used in the present investigation (23, p.235). The value for fulvic acid is lower than that given by Kononova, but the results reported by Kononova appear to have been obtained on the whole soil and not just on the surface horizons. Inclusion of lower horizons (e.g. B horizons) would probably

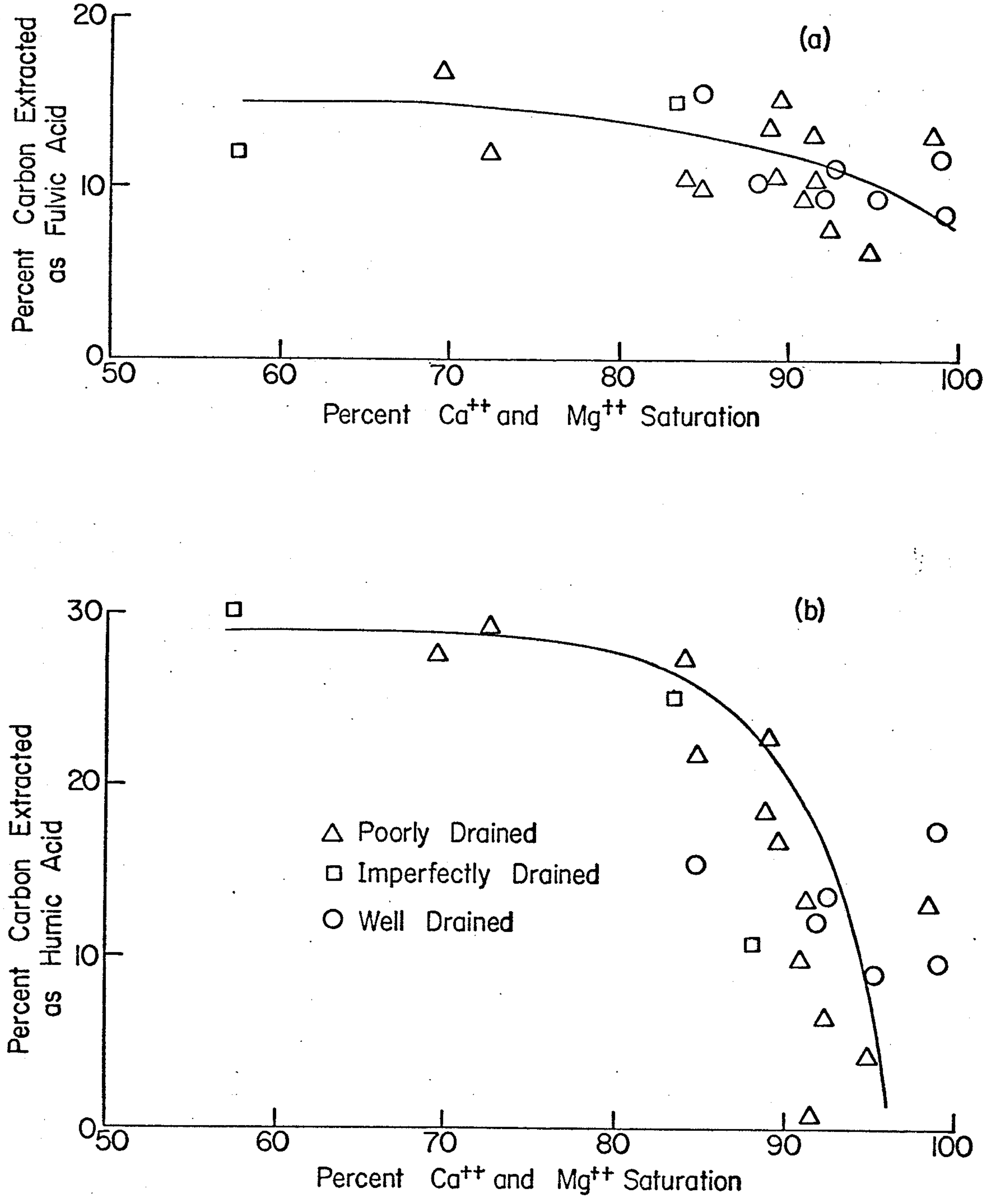

Figure 3 - EFFECT OF Ca^{++} AND Mg^{++} SATURATION OF EXCHANGE COMPLEX ON AMOUNT OF CARBON EXTRACTED AS (a) FULVIC ACID AND (b) HUMIC ACID

TABLE V

ORGANIC CARBON, ORGANIC MATTER AND EXTRACTABLE HUMIC ACID (E.H.A.)

Profile Type	Horizon	Thickness (inches)	% O.C.	% O.M.	% E.H.A.* in O.M.
Fera Humic Gleysol	L-F	3	22.6	38.9	26.2
	H	3	12.8	22.0	29.1
	Aheg	13	4.3	7.4	18.9
Low Humic Eluviated Gleysol	L-F	3	36.7	63.1	13.3
	H	1	21.2	36.5	23.8
	Aheg	3	5.5	9.5	28.4
	Aeg	6	0.8	1.4	-
Gleyed Grey Wooded	L-H	3	36.6	63.0	10.8
	Ahe	2	11.5	19.8	34.8
Gleyed Grey Wooded	Ap	6	2.7	4.6	26.1
Orthic Dark Grey	Ap	6	4.7	8.1	9.9
Orthic Dark Grey	L	½	49.7	85.5	12.2
	F-H	2	32.0	55.0	17.1
	Ahe	7	3.0	5.2	15.4
Rego Humic Gleysol	L-F	4	20.1	34.6	26.9
	Ahegl	2	3.7	6.4	20.3
	Aheg2	4	3.0	5.2	17.3
	Ahgl	6	3.1	5.3	11.3
	Ahg2	6	2.7	4.6	6.5
	Ahg3	10	2.1	3.6	5.6
Orthic Black	L-H	1	18.8	32.3	12.1
	Ah	7	5.4	9.3	9.7

* Extractable humic acid, calculated from percent soil organic carbon extracted as humic acid (Table I) and the carbon content of the humic acid (Table VI).

have made the value for fulvic acid higher since the organic matter of these horizons would probably be mainly fulvic acid.

The results indicate that the different drainages of these soils have little or no effect on the quantitative composition of the organic matter. It would seem that the factors affecting it are similar in all the soils investigated, possibly parent material and/or macro-climate. The surface horizons of poorly drained soils have the shortest period of saturation of all the horizons and it is here that organic matter formation and decomposition takes place. It is quite possible that for much of the time conditions in the surface horizons of poorly drained soils are no different from those in better drained soils. The only effect that poor drainage seems to have on the organic matter is that it causes a greater accumulation at the surface (Table V). This suggests that there is some decrease in the overall decomposition rate.

It is noticeable that the organic matter of the two Ap horizons appears to follow the trends established for the virgin soils.

Ash Contents of Humic Acids

The results presented in Table VI show that the ash contents of the humic acids vary considerably. In initial trials, with a few selected soils, the extracted humic acids were given a standardized treatment with HCl - HF solution which lowered the ash content to less than five percent. It appears that the choice of soils for the initial testing of the treatment was less than fortunate and the ash contents of the humic acids of the soils used in the investigation indicate that a standard procedure is of no use. Each sample must be treated individually if the ash contents are to be lowered to similar values. This would however raise the question of what effect the variation of treatments is likely to have

TABLE VI

ASH AND CARBON CONTENTS OF HUMIC ACIDS

Profile Type	Horizon	% Ash	% Carbon (Dry ash free basis)
Fera Humic Gleysol	L-F	7.96	60
	H	11.0	58
	Aheg	53.5	54
Low Humic Eluviated Gleysol	L-F	11.4	57
	H	16.0	56
	Aheg	31.0	43
Gleyed Grey Wooded	L-H	6.95	58
	Ahe	12.9	51
Gleyed Grey Wooded	Ap	12.4	55
Orthic Dark Grey	Ap	5.00	57
Orthic Dark Grey	L	1.28	65
	F-H	2.82	60
	Ahe	23.0	54
Rego Humic Gleysol	L-F	6.25	60
	Aheg1	35.2	47
	Aheg2	67.7	43
	Ahg1	42.4	53
	Ahg2	16.4	54
	Ahg3	4.85	57
Orthic Dark	L-F	1.52	59
	Ah	9.57	56

on the humic acid. Since the nature of a humic acid preparation is to some extent dependant on the method used to isolate and purify it, one must justify the use of different treatments before valid comparisons can be made between samples.

A noticeable trend is for the ash content to increase with depth and the concurrent decrease in organic matter. This suggests that as the organic matter content decreases a greater proportion of the humic acid that comes into solution with the NaOH extraction is associated with the mineral fraction. The general trend is reversed in the lower three horizons (Ah1, Ah2, Ah3) of the Rego Humic Gleysol. The ash contents of the humic acids decrease with increase in depth after a maximum of 67.7 percent had been reached in the Ahe2. It seems that the humic acids in these horizons are not as intimately associated with the mineral fraction as those in the upper horizons. These humic acids may be a more mobile fraction that has moved down the profile or they are less reactive.

Carbon Contents of Humic Acids

The carbon contents of the humic acids (Table VI) decrease with increased depth in the profile, with a reversal of the trend in the lower horizons (Ah1, Ah2, Ah3) of the Rego Humic Gleysol. The values are of the same order as those given by Dubach and Mehta (12) for humic substances, i.e. 46 - 65 percent. The lower values are generally obtained for fulvic acids whilst the higher ones are obtained for humic acids (23, pp.53 and 79; 34). Some of the humic acids have low carbon contents of the same magnitude as those associated with fulvic acids.

The carbon content is related to the molecular weight, the higher the carbon content the higher the molecular weight (16), thus the general trend in the soils investigated is for the molecular weight of the humic acids to decrease down the profile. The reversal of this trend in the lower three horizons (Ah1, Ah2, Ah3) of the Rego Humic Gleysol is not consistent with the previously suggested idea that the humic acids in these horizons represent a more mobile fraction. Mobility and molecular weight are inversely related, the lower molecular weight fractions (fulvic acids) being the most mobile. It is possible that the humic acids in the lower three horizons moved down the profile as low molecular weight substances and condensed into larger molecules in these horizons.

Functional Group Analysis of Humic Acids

The methods used for functional group analysis have been questioned as to the extent to which they comply with the theoretical assumptions on which their use is based. These criticisms must be borne in mind when interpreting the results of functional group analysis and for this reason a short discussion of the possible inadequacies will be given before the results of the present investigation are considered.

The assumption made, when using the calcium acetate method, is that only the more strongly acidic groups (carboxyl groups) will dissociate at the neutral to slightly acid pH of the calcium acetate solution. Actually the acidity of carboxyl and hydroxyl groups overlaps, for example 2,5 hydroxyquinone is more acidic than acetic acid (12). Thus the calcium acetate method only gives an accurate estimate of carboxyl groups if interfering groups are absent. Determination of carboxyl groups by reduction with diborane and the agreement of the results with the acidity measured by aqueous titration with NaOH to a pH of 8.5 lead, Dubach and Mehta (12) to rule out hydroxyquinones and enols as causes of acidity in the samples used. However, determination of carboxyl groups by the calcium acetate method give higher values, especially for samples with high hydroxyl group contents, and the authors suggest the possibility of chelate formation. Dijk (11) has reported that there are strong indications that, with humic acids, calcium ions can be linked to $-COO^-$ with one valency and $-O^-$ with the other. He considered the calcium acetate method to be quite inaccurate in this case.

In contrast to these views are those of Schnitzer and Gupta (35) who concluded that the calcium acetate method is suitable for the determination of carboxyl groups. They based their conclusion on the agreement between the values obtained by this method and those obtained by decarboxylation.

The barium hydroxide method as a means of estimating "total acidity" has been shown to give values in close agreement with those for active hydrogen determined by reduction with diborane (12). However, subtracting values for carboxyl groups from values of total acidity has been criticized as a means of estimating phenolic hydroxyls (16). Schnitzer and Gupta (35) feel that the difference between total acidity and carboxyl groups can be ascribed to the presence of phenolic hydroxyl groups, though they suggest the use of phenolic in quotation marks until more definite evidence is available.

The functional group values obtained in the present investigation (Table VII) were of the same order as those reported in the literature for similar organic matter preparations (16; 23,pp.52- 56; 34; 35). The results may be questioned as to their validity because of the high ash contents of the humic acids. Whether or not lowering the ash content would have altered the values was not investigated. However, had the estimation of the functional groups been affected by the ash content, it would be reasonable to expect the humic acids with the high ash contents

TABLE VII

FUNCTIONAL GROUP ANALYSIS OF HUMIC ACIDS

Profile Type	Horizon	Total Acidity* me/g	-COOH Groups* me/g	"Phenolic" -OH* me/g	OH/COOH	Equivalent Weight of Humic Acid
Fera Humic Gleysol	L-F	5.8	2.6	3.2	1.2	172
	H	6.9	2.8	4.1	1.5	145
	Aheg	7.1	3.0	4.1	1.4	141
Low Humic Eluviated Gleysol	L-F	6.1	2.7	3.4	1.3	164
	H	6.9	3.1	3.8	1.2	145
	Aheg	6.1	1.9	4.2	2.2	164
Gleyed Grey Wooded	L-H	5.6	2.4	3.2	1.3	179
	Ahe	6.0	2.4	3.6	1.5	167
Gleyed Grey Wooded	Ap	6.3	2.6	3.7	1.4	159
Orthic Dark Grey	Ap	6.1	3.1	3.0	1.0	164
Orthic Dark	L	4.7	1.7	3.0	1.8	213
	F-H	5.7	2.6	3.1	1.2	175
	Ahe	6.8	3.0	3.8	1.3	147
Rego Humic Gleysol	L-F	4.9	2.0	2.9	1.5	204
	Ahegl	5.4	1.9	3.5	1.8	185
	Aheg2	9.0	3.4	5.6	1.6	111
	Ahl	7.3	3.1	4.2	1.4	137
	Ah2	7.1	3.8	3.3	0.9	141
	Ah3	6.9	4.3	2.6	0.6	145
Orthic Black	L-H	5.4	2.9	2.5	0.9	185
	Ah	6.5	3.8	2.7	0.7	154

* Expressed on a dry, ash-free basis.

to have correspondingly low functional group values. This did not appear to be the case; in fact the humic acid with the highest ash content (67.7%) also had the highest "total acidity" (9.0 me/g).

The values for "total acidity" and the relative proportions of carboxyl and "phenolic" hydroxyl groups do not show any particular trends between the better drained and poorly drained soils. The "total" acidity" values are generally of similar magnitude for all the profiles and ratios of "phenolic" hydroxyls to carboxyls show random variation.

Individual horizons within each profile do show variations in both "total acidity" and the ratio of "phenolic" hydroxyl to carboxyl groups. Since all these soils have been subjected to some degree of leaching, it is reasonable to assume that there has been some movement of organic matter down the profile. The mobility of the organic matter and the severity of the leaching would govern the extent of organic matter movement and the concurrent fractionation. It is generally accepted that humic acids are not definite chemical compounds. Rather they are a mixture of different molecular weight fractions with the same solubility properties i.e. soluble in alkali, insoluble in acid. The acidity of humic substances decreases with increasing molecular weight (12) so it follows that the measured acidity of an humic acid preparation represents an average of the fractions it is composed of. An alteration of the proportions of the fractions would thus result in a change of the value. This change in the proportions of the fractions that make up the humic acid could be brought about in soils by leaching and this would cause variations in the acidity of humic acids from the different horizons within the profile.

If functional group analysis is to be used as a means of characterizing organic matter for the purpose of profile differentiation it may be better to take a core sample of the whole profile rather than samples of individual horizons. In this way the whole range of fractions that make up the humic acid of the profile are more likely to be present in their correct proportions.

Results discussed previously indicated that the amount of humic acid extracted is related to the degree of saturation of the exchange complex with Ca^{++} and Mg^{++}. The question can be raised as to whether or not the extracted humic acid is representative of that which is present in the soil. Undesireable fractionations occurring during manipulations have been suggested by Dubach and Mehta (12) as a possible reason for the difficulty in interpreting results of functional group analyses. The variation in extractability due to the effects of Ca^{++} and Mg^{++} could have caused undesireable fractionations.

It may be possible to attribute some of the variations that occur in the humic acids from different horizons to the degree of contamination with non humic substances. If fresh plant materials are extracted and fractionated by the procedure used for soil organic matter, fractions corresponding to humin, humic acid and fulvic acid will be obtained (26, p.160). Within a given profile contamination will presumably decrease with depth i.e. as one gets further away from the freshly added plant residues. The degree of contamination is also likely to vary between profiles depending on the type and amount of organic residues added. From the results in Table VII it can be seen that for each profile the horizons containing L and F material have the lowest "total acidities" and the values differ between profiles.

Equivalent weights of the humic acids were calculated from the values for "total acidity" (Table VII). Equivalent weight = $\frac{1000}{\text{Total acidity (me/g)}}$. The relationship between equivalent weight and percent carbon in the humic acid as shown in Figure 4. Except for four points there is a trend for the equivalent weight to increase as percent carbon increases. The linear correlation is significant ($r = 0.53$) at the 5 percent level.

The carbon contents of the four samples would lead one to expect higher total acidities (12). If the acidities of these samples were higher the equivalent weights would be lower. However the carbon contents of these samples are lower than those usually associated with humic acids. The values of 43% carbon for two of the samples are more like the values obtained for fulvic acids (34) and the high total acidities that would be required to bring them into line with the rest of the samples would also be more like those associated with fulvic acids. It appears that these samples may be different from the rest.

The trend for equivalent weight to increase with percent carbon is in agreement with the observations that an increase in percent carbon is associated with an increase in molecular weight which in itself is associated with an increase in equivalent weight (12).

If one can assume that the results of the functional group analyses accurately reflect the real nature of the humic acids they do not show differences which distinguish the poorly drained from the better drained soils. The conclusion that is drawn from this is that, in the soils studied, variations in the moisture regimes (and the associated variations in vegetation) do not appear to influence the nature of the humic acids formed. This would be in agreement with the conclusion of Flaig (17) that the properties of humic acids are relatively similar

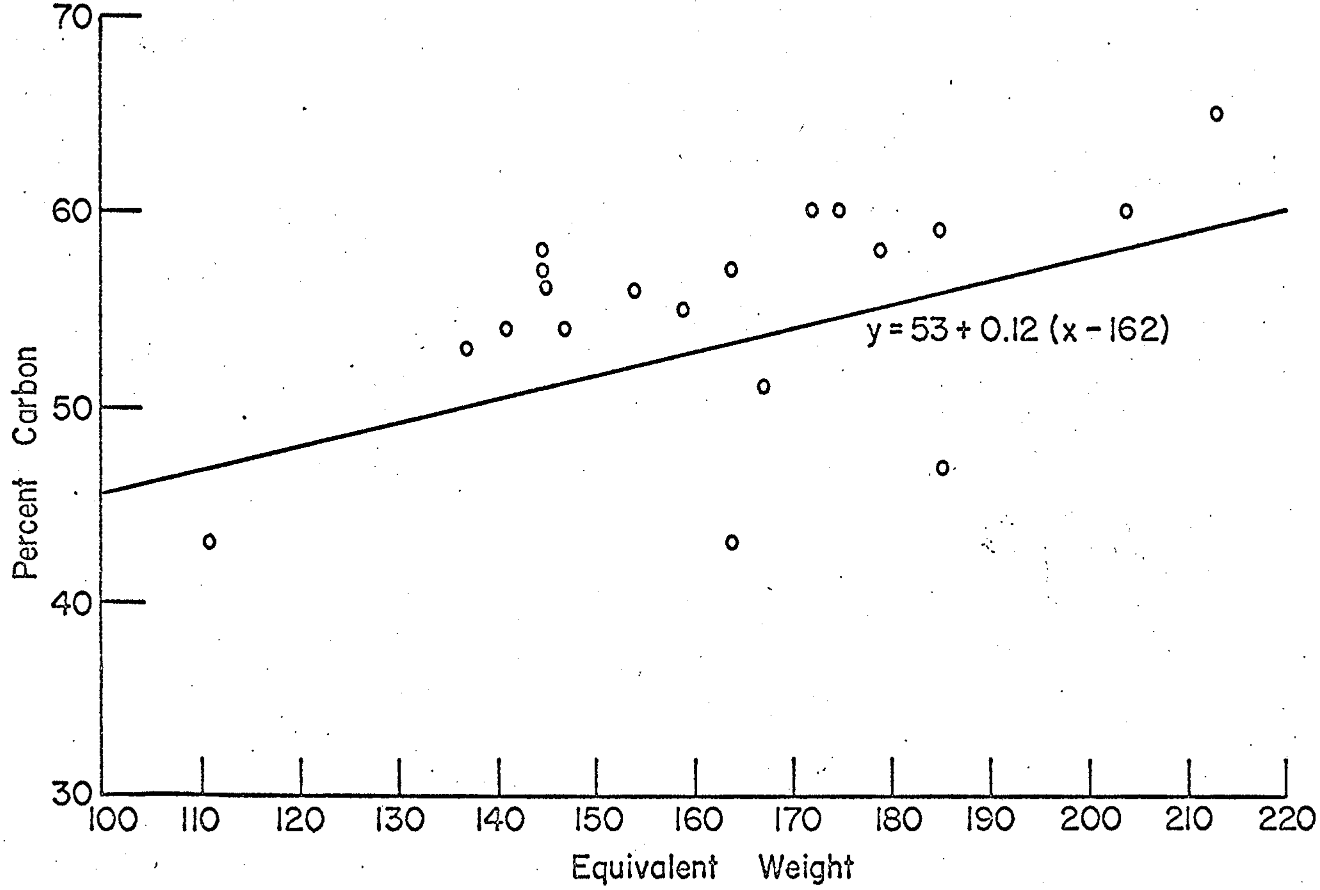

Figure 4 - RELATIONSHIP BETWEEN CARBON CONTENT AND EQUIVALENT WEIGHT OF HUMIC ACIDS.

even though they have developed from very different materials and under a variety of external conditions. This view has also been expressed by other workers (4; 40).

In view of the divergent opinions on the validity of results obtained by the methods used for functional group analyses one is not justified in saying that differences do not exist. The failure to find differences may possibly be attributable to the inadequacies of the analytical procedures used. It should be borne in mind that humic acid preparations are not discrete compounds but mixtures whose composition will depend upon the state in which they exist in the soil and the method used to isolate them.

V SUMMARY AND CONCLUSIONS

The purpose of this investigation was to determine whether the organic matter in well drained soils differed from that of associated soils of poorer drainage. The amount of organic matter extracted by 0.5N NaOH and the proportions of humic and fulvic acids in the extract were determined to assess the quantitative composition of the organic matter. The "total acidity" and carboxyl group content of the humic acid fraction were determined to learn something about their chemical nature. The methods used for functional group analysis were ones that could be adopted for routine analysis.

From the results obtained, the following conclusions were drawn:-

1. The amounts of organic matter extracted by 0.5N NaOH were not related to the soil type. The amount of NaOH extractable organic matter was related to the degree of saturation of the exchange complex with Ca^{++} and Mg^{++}. The extractability of the humic acid fraction was influenced to a much greater extent than the fulvic acid fraction. Extrapolation of the results indicated that, if the effect of Ca^{++} and Mg^{++} was removed, approximately the same proportions of humic to fulvic acids would be extracted from all the soils investigated.

2. Extraction of organic matter with 0.5N NaOH does not give a very good indication of the amount of humic acid in the soils studied. It would seem that pretreatment of the soil with acid or the use of a complexing reagent e.g. alkaline sodium pyrophosphate would be better. This would overcome the effect of Ca^{++} and Mg^{++}.

3. Functional group analysis indicates that the humic acids extracted from the soils are similar. Variations between horizons in each profile are possibly the result of the different mobilities of the

various components of the organic matter. Leaching would cause fractionation, the more mobile components moving further down the profile.

4. The similarity of the quantitative composition and functional group content indicate that the differences in the environmental conditions due to the different drainages have not influenced the nature of the organic matter formed in the soils investigated.

VI BIBLIOGRAPHY

1. Allison, L. E. 1965. Organic Carbon, in Methods of Soil Analysis. Part 2. C. A. Black, et al. editors. Am Soc. Agron., Madison, Wis. pp.1367 - 1378.

2. Atkinson, H. J., Giles, G. R., MacLean, A. J. and Wright, J. R. 1958. Chemical Methods of Soil Analysis. Can. Dept. Agr., Ottawa.

3. Ball, D. F. 1964. Loss on ignition as an estimate of organic matter and organic carbon in non-calcareous soils. J. Soil Sci. 15: 84 - 92.

4. Bartholomew, W. V. 1966. The role of micro-organisms in the formation and decomposition of organic compounds in soil, in "The Use of Isotopes in Soil Organic Matter Studies. Rep.F.A.O./I.A.E.A. tech. Meet. Brunswick-Völkenrode, 1963. Pergamon Press, Toronto.

5. Bremner, J. M. 1954. A review of recent work on soil organic matter. II. J. Soil Sci. 5: 214 - 232.

6. Bremner, J. M. 1965. Organic Nitrogen in Soils, in Soil Nitrogen. W. V. Bartholomew and F. E. Clark ed. Am. Soc. Agron., Madison, Wis. p.93 - 149.

7. Bremner, J. M. and Lees, H. 1949. Studies on soil organic matter. Part 2. The extraction of organic carbon and nitrogen from soil. J. Agr. Sci. 39: 274 - 270.

8. Broadbent, F. E. 1953. The soil organic fraction. Adv. Agron. V: 153 - 183.

9. Buckman, H. O. and Brady, N. C. 1960. The Nature and Properties of Soils. 6th ed. The MacMillan Company, New York.

10. Davies, R. I. and Coulson, B. C. 1959. Humic Acid. A letter to the editor. Soils and Fert. 22: 159.

11. Dijk, H. van. 1966. Some physico-chemical aspects of the investigation of humus, in The Use of Isotopes in Soil Organic Studies. Rep.F.A.O./I.A.E.A. tech. Meet. Brunswick-Völkenrode, 1963. Pergamon Press, Toronto, p.129 - 141.

12. Dubach, P. and Mehta, N. C. 1963. The chemistry of soil humic substances. Soils and Fert. 26: 293 - 300.

13. Ehrlich, W. A., Pratt, L. E., and Leclaire, F. P. 1959. Report of reconnaissance soil survey of Grandview map sheet area. Manitoba Department of Agriculture.

14. Ehrlich, W. A., Pratt, L. E., and Poyser, E. A. 1956. Report of reconnaissance soil survey of Rossburn and Virden map sheet areas. Manitoba Department of Agriculture.

15. Farmer, V. C., and Mitchell, B. D. 1963. Occurrance of oxalates in soil clays following hydrogen peroxide treatment. Soil Sci. 4: 221-229.

16. Felbeck, G. T, Jr. 1965. Structural chemistry of soil humic substances. Adv. Agron. XVII: 327-368.

17. Flaig, W. 1966. The chemistry of humic substances, in The Use of Isotopes in Soil Organic Matter Studies. Rep.F.A.O./I.A.E.A. tech. Meet. Brunswick-Völkenrodge. 1963. Pergamon Press, Toronto. p.103-127.

18. Heald, W. R. 1965. Calcium and Magnesium, in Methods of Soil Analysis Part 2. C. A. Black, et al. editors. Am. Soc. Agron., Madison, Wis. p.999-1010.

19. Jackson, M. L. 1956. Soil Chemical Analysis-Advanced Course. Published by the author, Dept. of Soils, University of Wisconsin, Madison, Wis.

20. Jackson, M. L. 1958. Soil Chemical Analysis. Prentice-Hall Inc., Englewood Cliffs, N.J.

21. Joffe, J. S. 1949. Pedology Publications, New Brunswich, N.J.

22. Kilmer, V. J., and Alexander, L. T. 1949. Methods of making mechanical analyses of soils. Soil Sci. 68: 15-24.

23. Kononova, M. M. 1961. Soil Organic Matter. Pergamon Press, Toronto.

24. Levesque, M., and Schnitzer, M. 1966. Effects of NaOH concentration on the extraction of organic matter and of major inorganic constituents from a soil. Can. J. Soil Sci. 46: 7-12.

25. Levesque, M., and Schnitzer, M. 1967. The extraction of soil organic matter by base and chelating resin. Can. J. Soil Sci. 47: 76-78.

26. Marshall, C. E. 1964. The Physical Chemistry and Mineralogy of Soils. Vol. 1. Soil Materials, John Wiley and Sons, Inc., N.Y.

27. Mortensen, J. L., and Himes, F. L. 1964. Soil Organic Matter in Chemistry of the Soil. F. E. Bear, ed. Reinhold Publishing Corp., N. Y. pp.206-241.

28. National Soil Survey Committee (Canada). 1967. Rep. 6th Nat. Meet., Quebec, 1965. Can. Dept. Agr., Ottawa.

29. Ponomareva, V. V., and Plotnikova, T. A. 1967. Data on the degree of intramolecular oxidation of humus in various soil groups (Problem of the carbon to humus conversion factor). Soviet Soil Sci. 7: 924-933.

30. Russell, E. W. 1961. Soil Conditions and Plant Growth. Longmans, London.

31. Schnitzer, M. 1967. Humic-fulvic acid relationships in organic soils and humification of the organic matter of these soils. Can. J. Soil Sci. 47: 245- 250.

32. Schnitzer, M., and Desjardins, J. G. 1965. Carboxyl and phenolic hydroxyl groups in some organic soils and their relation to the degree of humification. Can. J. Soil Sci. 45: 257- 264.

33. Schnitzer, M. and Desjardins, J. G. 1966. Oxygen-containing functional groups in organic soils and their relation to the degree of humification as determined by solubility in sodium pyrophosphate solution. Can. J. Soil Sci. 46: 237- 243.

34. Schnitzer, M. and Gupta, U. C. 1964. Some chemical characteristics of the organic matter extracted from the O and B_2 horizons of a Gray Wooded Soil. Soil Sci. Soc. Am. Proc. 28: 374- 377.

35. Schnitzer, M. and Gupta, U. C. 1965. Determination of acidity in soil organic matter. Soil Sci. Soc. Am. Proc. 29: 274- 277.

36. Schnitzer, M., and Hoffman, I. 1966. A thermogravimetric approach to the classification of organic soils. Soil Sci. Am. Proc. 30: 63 - 66.

37. Schnitzer, M., and Wright, J. R. 1957. Extraction of organic matter from Podzolic soils by means of dilute inorganic acids. Can. J. Soil Sci. 37: 89- 95.

38. Schnitzer, M., Wright, J. R., and Desjardins, J. G. 1958. A comparison of the effectiveness of various extractants for organic matter from two horizons of a Podzol profile. Can. J. Soil Sci. 38: 49- 55.

39. Schofield, R. K., and Taylor, A. W. 1955. The measurement of soil pH. Soil Sci. Soc. Am. Proc. 19: 164- 167.

40. Sowden, F. J., and Atkinson, H. J. 1949. The composition of certain soil organic matter fractions. Soil Sci. 68: 433- 440.

41. Tinsley, J., and Salam, A. 1961. Extraction of soil organic matter with aqueous solvents. Soils and Fert. 24: 81- 84.

42. Waksman, S. A. 1936. Humus: Origin, Chemical Composition and Importance in Nature. Williams and Wilkins, Baltimore, Maryland.

43. Wright, J. R., Schnitzer, M., and Levick, R. 1958. Some characteristics of the organic matter extracted by dilute inorganic acids from a Podzolic B horizon. Can. J. Soil Sci. 38: 14- 22.

44. Yuan, T. L. 1964. Comparison of reagents for soil organic matter extraction and effect of pH on subsequent separation of humic and fulvic acids. Soil Sci. 98: 133- 141.

APPENDIX

Comparison of Methods for Determination of Total Organic Matter

Methods. Total organic matter was determined by the following methods:

(i) The values for percent organic carbon were multiplied by 1.72 (20, p.221).

(ii) The soils were oven dried at 105° C and ignited in a muffle furnace at 375° C for sixteen hours. The loss in weight of the oven dried sample was taken as organic matter (3).

(iii) The soils were oven dried at 105° C and treated with hydrogen peroxide in a manner similar to the pretreatment used for mechanical analyses (22). Total organic matter was taken as the loss in weight on an oven dry basis.

Discussion. In the majority of cases estimates of the organic matter contents of soils are obtained by determining the percent organic carbon and multiplying by a factor, usually 1.724 (8). It has been shown that the value of the factor can vary from 1.6 to 3.3 for different soils (8), and for general use values of 1.9 - 2.5 have been suggested (8; 29). The other approach to estimating total organic matter is to destroy it and determine the loss in weight.

Destruction of organic matter can be brought about by oxidation with hydrogen peroxide or ignition in a muffle furnace. Both methods are considered by Broadbent (8) to be of little value. However, Jackson (20, pp.222-225) describes a method utilizing hydrogen peroxide oxidation which he considers to be useful and Ball (3) has shown that loss on ignition is a good estimate of organic matter. Because there is so much disagreement on the best way of estimating the total organic matter content of a soil, the three approaches were tried.

The values for the three different estimates of total organic matter are presented in Table VIII. Percent loss on ignition and percent loss on peroxide treatment correlate linearly very well with percent organic carbon, r = 0.9** in both cases (Figures 5 and 6). The values for organic matter by peroxide oxidation are lower than those by loss on ignition and organic carbon x 1.72. In many cases the values for loss on peroxide treatment are lower than the percent organic carbon. Determination of the organic carbon content of the residues indicated that in the majority of cases almost 100 percent of the carbon had been oxidized by the hydrogen peroxide (Table IX) the lowest value being 91 percent. During the determination of organic carbon in the residues, it was noticed that effervesence occurred when the H_2SO_4 was added. This suggested that some carbon was in the residue and was being oxidized to CO_2. If the carbon in the residue is in a highly oxidized state very little dichromate would be required to oxidize it to CO_2. Malonic and oxalic acids have been shown to be products of peroxide oxidation (15; 16) and both these compounds have a high oxygen content. From the results, it was concluded that determining loss on peroxide treatment by the method used was of little use as a means of estimating the total organic matter content of soils.

Percent loss of ignition shows much better agreement with percent organic carbon x 1.72. The percent loss on ignition for organic horizons is equal to or less than percent organic carbon x 1.72 which suggests that the carbon content in several cases is higher than that upon which the value of the factor is based. On the other hand the percent loss on

---

** Significant at 0.01 level.

TABLE VIII

ORGANIC MATTER, LOSS ON IGNITION AND LOSS ON PEROXIDE TREATMENT.

Profile Type	Horizon	% O.M. (% O.C. x 1.72)	% Loss on Ignition	% Loss on Peroxide Treatment
Fera Humic Gleysol	L-F	38.9	38.9	28.0
	H	22.0	21.9	14.6
	Aheg	7.4	7.9	0.5
Low Humic Eluviated Gleysol	L-F	63.1	55.7	49.2
	H	36.5	33.2	22.9
	Aheg	9.5	10.0	5.7
Gleysol Grey Wooded	L-H	63.0	56.7	49.5
	Ahe	19.8	18.5	14.5
Gleyed Grey Wooded	Ap	4.6	5.6	1.0
Orthic Dark Grey	Ap	8.1	8.7	4.1
Orthic Dark Grey	L	85.5	-	73.1
	F-H	55.0	53.7	47.3
	Ahe	5.2	6.8	1.5
Rego Humic Gleysol	L-F	34.6	34.5	27.7
	Ahegl	6.4	7.9	2.6
	Aheg2	5.2	7.1	1.0
	Ahgl	5.3	7.4	1.5
	Ahg2	4.6	6.1	2.1
	Ahg3	3.6	5.4	2.1
Orthic Black	L-H	32.3	31.3	26.0
	Ah	9.3	10.3	5.2

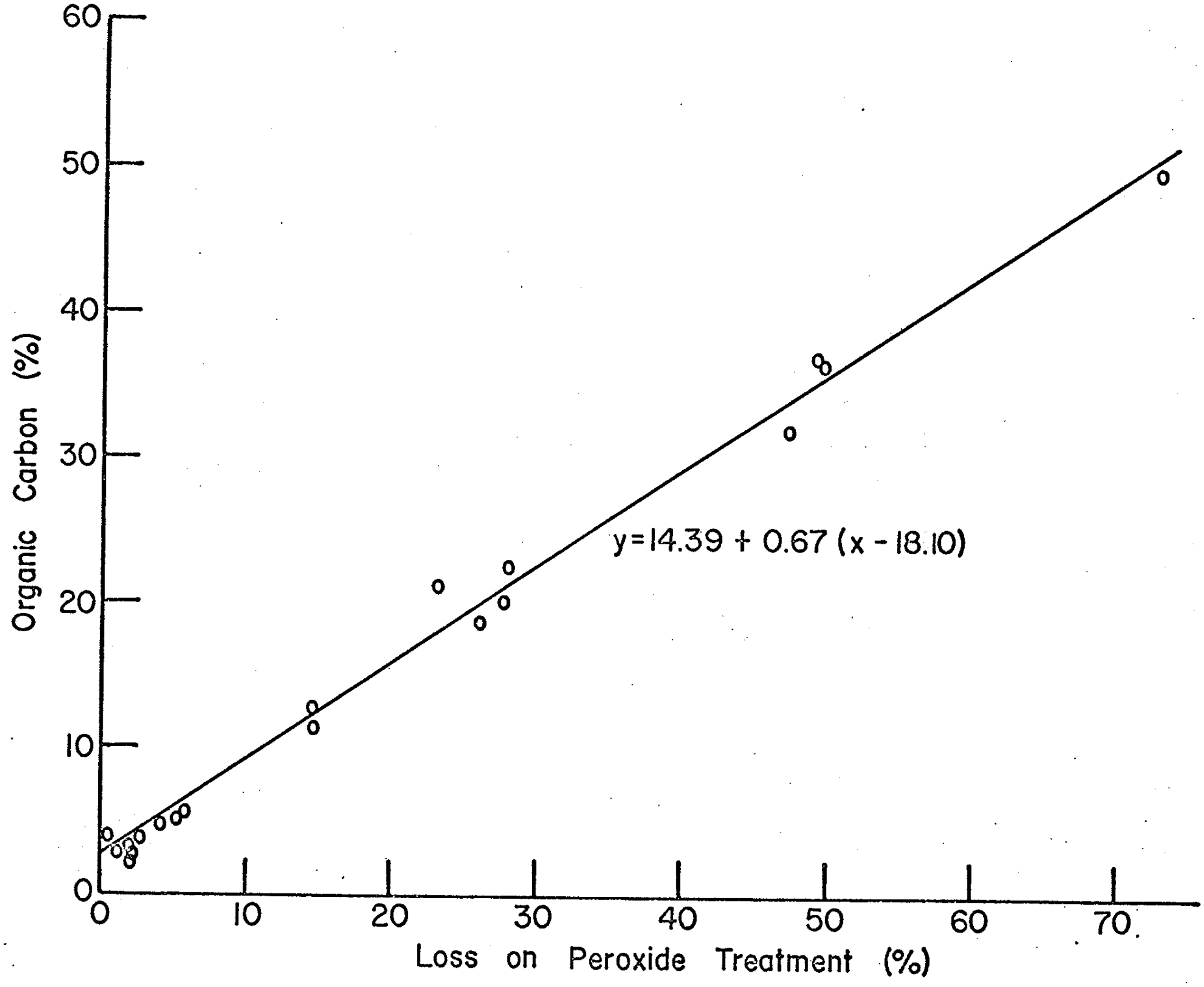

Figure 5 - RELATIONSHIP BETWEEN LOSS ON PEROXIDE TREATMENT AND ORGANIC CARBON CONTENT OF SOILS.

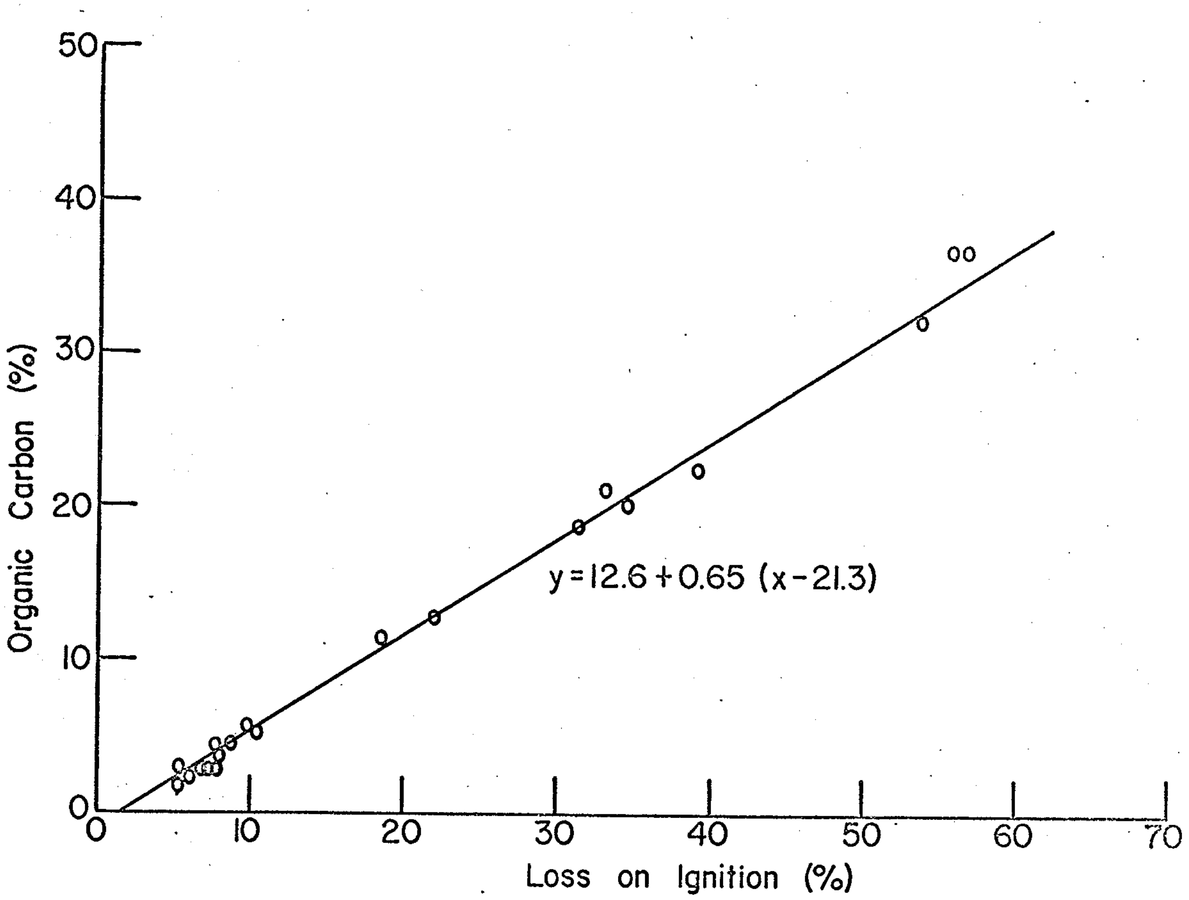

Figure 6 - RELATIONSHIP BETWEEN LOSS ON IGNITION AND ORGANIC CARBON CONTENT OF SOILS.

TABLE IX

PERCENT ORGANIC CARBON OXIDIZED BY HYDROGEN PEROXIDE

Profile Type	Horizon	% O.C. in residue (based on original wt. of soils)	% O.C. oxidized
Fera Humic Gleysol	L-F	1.44	94
	H	1.18	91
	Aheg	0.33	92
Low Humic Eluviated Gleysol	L-F	1.40	96
	H	0.70	97
	Aheg	0.10	98
Gleyed Grey Wooded	L-H	0.47	99
	Ahe	0.15	99
Gleyed Grey Wooded	Ap	0.07	97
Orthic Dark Grey	Ap	0.13	97
Orthic Dark Grey	L	0.43	99
	F-H	0.73	98
	Ahe	0.04	99
Rego Humic Gleysol	L-F	0.13	99
	Ahegl	0.04	99
	Aheg2	0.07	98
	Ahgl	0.04	99
	Ahg2	0.04	99
	Ahg3	0.04	98
Orthic Black	L-H	0.77	96
	Ah	0.13	98

ignition values for the mineral horizons, which have a relatively low content of organic matter, are generally higher than percent organic carbon x 1.72. This is probably, in the main, due to loss of structural water which is relatively large in comparison to the organic matter content. In Figure 2 extrapolation of the regression line to zero percent organic carbon gives a percent loss on ignition of 1.9 percent. Subtracting this value from the percent loss on ignition for the mineral horizons gives better agreement with percent organic carbon x 1.72 in several cases, especially for the Rego Humic Gleysol. However this loss of structural water is not constant but will vary according to the type and quantity of clay present (3).

The results indicate that percent loss on ignition and percent organic carbon x 1.72 give reasonably good agreement as estimates of total organic matter for the soils investigated. Loss on ignition is probably better for soils with a low content of mineral colloids whilst percent organic carbon x 1.72 should be used if the content is high. Loss on ignition can be used on soils with a high content of mineral colloids if the soil is first pretreated with a mixture of HCl and HF to break down the hydrated mineral matter. This method, proposed by Rather, suffers from the fact that it is time consuming which makes it unsuitable for routine work (8).

It was decided to utilize the values for percent organic matter obtained from percent organic carbon x 1.72 since loss on ignition gave no greater accuracy.